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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

# *TRINITROPHENYLMALONIC ESTER: SECOND PAPER.*

BY C. LORING JACKSON AND J. I. PHINNEY.

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# TRINITROPHENYLMALONIC ESTER.

## SECOND PAPER.

BY C. LORING JACKSON AND J. I. PHINNEY.

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THE work described in this paper was undertaken with the intention of preparing some derivatives of the trinitrophenylmalonic ester (picrylmalonic ester), $C_6H_2(NO_2)_3CH(COOC_2H_5)_2$, discovered by C. A. Soch and one of us.* It has led to the discovery of a second and more stable form of the trinitrophenylmalonic ester, which melts at 64° instead of 58°, the melting point of the form at first obtained; and we have also prepared the nitrite of this ester,

$$C_6H_2(NO_2)_3CNO_2(COOC_2H_5)_2,$$

melting at 109°, the corresponding trinitrophenyltartronic ester,

$$C_6H_2(NO_2)_3COH(COOC_2H_5)_2,$$

melting at 117°, its acetyl derivative,

$$C_6H_2(NO_2)_3COCOCH_3(COOC_2H_5)_2,$$

which melts at 125°, and the trinitrophenylacetic acid,

$$C_6H_2(NO_2)_3CH_2COOH,$$

melting at 161°.

### *The Two Modifications of Trinitrophenylmalonic Ester.*

The trinitrophenylmalonic ester, as prepared by Soch and one of us,† crystallized from alcohol in white long rather slender rectangular plates, or when better developed in thick prisms with blunt ends, often as much as two centimeters long. It melted at 58°.‡ When we first took up the

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* These Proceedings, XXX. 401.

† Ibid.

‡ In the previous paper, this melting point is given as 59°, but it must be changed to 58°, as it was found after that paper was published that the zero point of the thermometer used had changed.

work again, we also obtained the trinitrophenylmalonic ester exclusively in this form, and confirmed repeatedly the observations given above on its crystalline form and melting point. Somewhat later we converted a sample of the trinitrophenylmalonic ester into its very characteristic ammonium salt, and upon acidifying this and recrystallizing the ester thus set free we obtained instead of the rectangular plates four- (or six-) sided plates in which two of the opposite angles were unlike, — one being obtuse and the other acute, — so that the crystals were shaped somewhat like a kite; and not only did the form of these crystals differ in such a marked way from the rectangular plates previously obtained, but they also melted at 64° instead of at 58°. During this experiment a solution of the ester from one of our preparations of it was evaporating spontaneously on the desk; the next morning these kite-shaped crystals were deposited from it, although it had previously yielded only the rectangular plates melting at 58°, and since then we have obtained from all our preparations only the form melting at 64°, whereas before exactly similar preparations had given us exclusively the form melting at 58°, as has been already stated. Varying the conditions of the preparations, such as carrying them on in cooled or warmed solutions, or with longer or shorter standing, did not modify the result, so that we have not succeeded in adding to the stock of the modification melting at 58°, which we had on hand, when we encountered the other form.

The following experiment seems to us to suggest a possible explanation of these results: a solution of the form melting at 58° was evaporated until it began to deposit the rectangular crystals, and then inoculated with a speck of the form melting at 64°, when at once the kite-shaped crystals of this form began to appear, and no more rectangular crystals were produced. This experiment was tried several times early in our work; it could not be repeated later, as then recrystallization alone of the form melting at 58° was enough to convert it partially or even completely into the form melting at 64°. As then a small amount of the form melting at 64° is enough to convert a large quantity of the other form into this, it seems probable that the small amount of the more stable form floating in the air of the laboratory as dust was enough to bring about this change, and to give us this more stable modification as the sole product of our preparations, and even of recrystallizations of the less stable form. The view that the inoculation of the solutions proceeded from the dust in the air is supported by the following observations. A preparation made with new apparatus and fresh material, but in the laboratory where these experiments had been tried, yielded

only the stable form melting at 64°. Crystallizations of the form melting at 58° gave, after the work had been in progress some time, the form melting at 64°. We then crystallized a specimen melting at 58° in a fresh room, which had not been used for these experiments, and obtained in this way the rectangular plates melting at 58°; but upon recrystallizing the specimen, the form melting at 64° appeared, and after this the first crystallization of a fresh specimen melting at 58° in this room gave crystals of the form melting at 64°. A probable explanation of these latter observations is that there was a little dust of the more stable modification in this room coming from the clothes of one of us, who used it as a lecture room, and that this was sufficient gradually to inoculate the solutions. As the laboratory building, apparently contaminated with the dust of the more stable form, seemed to offer little chance of preparing more of the form melting at 58°, we postponed publishing this paper for some years, in the hope that one of us (who left Cambridge at the end of the year) might prepare more of the form melting at 58° by working in entirely new surroundings. Unfortunately, the pressure of other duties has prevented the carrying out of this work, and we have decided that it is wiser to publish now the results already obtained rather than to postpone the appearance of the paper to a still later date.

The conversion of the form melting at 58° into that melting at 64° has been brought about by us in the following ways. By its conversion into the ammonium salt and setting free the ester by acidification; * by inoculating a saturated alcoholic solution with a crystal of the form melting at 64°; by melting the less stable form it was partially changed into that melting at 64°, and, if the melting was repeated, the change became complete. It is possible, however, that this change might have been due to inoculation from dust. On the other hand, we have not succeeded in converting the form melting at 64° into that melting at 58° in spite of many experiments; even melting the more stable form and stirring it with a rod tipped with the modification melting at 58° did not have the desired effect.

The substance melting at 64° was purified by crystallization from alcohol, and after being dried *in vacuo* was analyzed with the following results: —

I. 0.2050 gram of the substance gave on combustion 0.3149 gram of carbonic dioxide and 0.0736 gram of water.

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* In my earlier work with Soch, the sodium salt yielded on acidification the ester melting at 58°. — C. L. J.

II. 0.2007 gram of substance gave 0.3078 gram of carbonic dioxide and 0.0789 gram of water.

III. 0.2040 gram of substance gave 20.5 c.c. of nitrogen at a temperature of 21° and a pressure of 759.6 mm.

| | Calculated for $C_6H_2(NO_2)_3CH(COOC_2H_5)_2$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Carbon | 42.05 | 41.89 | 41.82 | |
| Hydrogen | 3.50 | 3.98 | 4.36 | |
| Nitrogen | 11.32 | | | 11.41 |

The combustion of this substance must be carried on as slowly as possible, as it has a strong tendency to explode.

The molecular weight of the substance was also determined by the method of Raoult with the following results: —

I. Weight of benzol used 19.2120 grams, substance 0.3291 gram. Reduction of freezing point 0°.230.

II. Weight of benzol used 15.7244 grams, substance 0.3428 gram. Reduction of freezing point 0°.306.

III. Weight of benzol used and weight of substance the same as in II. Reduction of freezing point 0°.297.

| | Calculated for $C_6H_2(NO_2)_3CH(COOC_2H_5)_2$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Molecular Weight | 371 | 365.1 | 349.0 | 359.6 |

From these results there can be no doubt that the preparation melting at 64° was trinitrophenylmalonic ester.

It is worth while to point out here that the form melting at 58° could not have owed its peculiarities in melting point and crystalline form to the presence of a small quantity of some impurity, since it was repeatedly brought to a constant melting point both by Dr. Soch and by us; and, if this explanation were correct, this form should have been the first product of the preparations in our later work, whereas, after we had once obtained the form melting at 64°, we could not prepare the other. Dr. Soch's analyses of the form melting at 58° also show that it was pure.

| | Calculated. | Found. | |
|---|---|---|---|
| Nitrogen | 11.32 | 11.75 | 11.38 |

We are therefore led to the conclusion that the trinitrophenylmalonic ester exists in two isomeric forms.

The isomerism of these two forms is probably due to the same cause as that of the red and yellow anilidotrinitrophenyltartronic esters (melt-

ing at 143° and 122°) discovered by W. B. Bentley * and one of us. It seems more doubtful whether it is related to the isomerism of the formylphenylacetic esters discovered by W. Wislicenus,† of the dibenzoylacetones ‡ and the benzoates of oxymethylenacetone § of Claisen, and the benzalanilinacetacetic esters of R. Schiff,¶ since both of our isomeres can be dissolved in alkaline solutions without alteration, whereas one of the most marked differences between the isomeres in these other cases consists in the fact that one dissolves in alkalies and the other does not.

Our present knowledge of these substances is not sufficient to allow us to make a final statement in regard to the cause of this isomerism, but the following discussion may be given for what it is worth. The fact that each form has been converted into a salt, and set free from this unaltered upon acidification, would indicate that it is a case of chemical rather than physical isomerism; and, if this is true, as the symmetrical nature of the substance would forbid stereometric isomeres, the only probable explanation which we have been able to find is that the isomerism depends on differences of structure in the malonic group, as indicated by the following formulas: —

$$\text{I.}\quad C_6H_2(NO_2)_3CH(COOC_2H_5)_2.$$

$$\text{II.}\quad C_6H_2(NO_2)_3C\begin{matrix} \diagup COOC_2H_5. \\ = COH.OC_2H_5. \end{matrix}$$

In other words, that the isomerism is analogous to that of the bodies studied by W. Wislicenus, Claisen, and R. Schiff. There are, however, objections to this explanation, and, as we have said already, the whole subject needs further investigation before any theory can be found satisfactory.

*Properties of the Trinitrophenylmalonic Ester melting at* 64°. — Crystallized from alchohol, it forms white plates, usually bounded by four or six sides. In the four-sided form there are two unlike opposite angles, one obtuse the other acute, which give a very characteristic appearance to the crystals. The six-sided form is produced by two planes truncating the similar angles in the four-sided form. Both these forms resemble a kite in shape. Occasionally much more complex crystals were observed, having a parallel-sided projection arising from the middle of the obtuse end, and also terminated by an obtuse angle; this form had a general resemblance to the "spade" in playing cards. The plates

* These Proceedings, XXVI. 82.

† Ber. d. chem. Ges., 1895, p. 767.

‡ Ann. Chem., CCLXXVII. 188.

§ Ber. d. chem. Ges., XXV. 1785.

¶ Ber. d. chem. Ges., XXXI. 601.

were often thick, especially when having the complex form last described. The substance turns yellow on long exposure to the air, and imparts to alcohol a marked crimson color, which has also been observed on the ground glass stopper of the bottle in which it was kept. In this case the color may have been due, however, to some alkali from the glass, but this was not the case in the alcoholic solution, as the color was only partially discharged by acidification. The modification melting at 58° forms similar crimson solutions. It melts at 64° to a red liquid. Its solubility in the organic solvents is essentially the same as that of the form melting at 58° ; that is, it is very soluble in chloroform, ether, benzol, or glacial acetic acid; somewhat less so in carbonic disulphide; soluble in cold alcohol, freely in hot, rather more soluble in methyl than in ethyl alcohol; insoluble in ligroine, or cold water, slightly soluble in hot water.

The action of acids upon this more stable trinitrophenylmalonic ester is described in some of the following paragraphs of this paper. Alkalies give with it dark red salts, which crystallize well. The ammonium salt is especially characteristic; it was made by adding an excess of aqueous ammonic hydrate to a warm nearly saturated alcoholic solution of the trinitrophenylmalonic ester. The solution took on a deep purplish red color, and in a few seconds the whole solidified to a thick semisolid mass having the purplish red color and consistency of clotted blood. A microscopic examination showed that this mass was made up of long very slender hair-like crystals, which after drying had a rich golden brown color and a silky lustre. The salt decomposed below 100°, at first turning black, but afterward melting to a clear yellowish liquid, which exploded at higher temperatures. It is rather sparingly soluble in water; soluble in alcohol, chloroform, or acetone; insoluble in ligroine. The solutions have a dark red color, but if the solution in water or alcohol is boiled for some time it turns yellowish brown; unfortunately no product could be obtained from such solutions in a state fit for analysis.

An aqueous solution of the ammonium salt gave the following characteristic precipitates.

With salts of barium an abundant crystalline amethystine precipitate.

With salts of strontium a dark red precipitate.

With salts of calcium a brick-red precipitate.

With salts of zinc an abundant crystalline scarlet precipitate, turning to reddish brown on standing.

With salts of cadmium a granular scarlet precipitate.

With salts of copper a heavy flaky precipitate, varying from reddish yellow to brownish red.

With salts of lead heavy dark red flocks.

Salts of the other metals gave precipitates as a general rule, but they were not characteristic. The behavior with argentic nitrate, however, should be especially mentioned, as this gave no precipitate in dilute solutions, and only a slight cloudy dark red one when the solutions were strong. The barium, zinc, and copper salts were analyzed.

*Barium Salt.* — This salt was made by adding a solution of baric chloride to the aqueous solution of the ammonium salt. The heavy purple flocks thus obtained were washed with water, dried at 100°, and analysed with the following result: —

0.4864 gram of the salt gave 0.1236 gram of baric sulphate.

| | Calculated for $[C_6H_2(NO_2)_3C(COOC_2H_5)_2]_2Ba$. | Found. |
|---|---|---|
| Barium | 15.62 | 14.95 |

The salt is so hygroscopic that two tenths of a gram will gain as much as four milligrams during the time of weighing, if it is in an open watch glass. In evaporating it with sulphuric acid for analysis, care must be taken not to apply the heat too suddenly at first, or an explosion may result. The best plan is to heat the mixture for some time to 100°, as then the decomposition goes on quietly.

*Properties.* — The barium salt appears as a purple obscurely crystalline mass, essentially insoluble in water. It explodes if heated to 120°.

*Zinc Salt.* — This salt was made by mixing solutions of zincic sulphate and the ammonium salt of the ester. It was purified by washing, dried at 100°, and analyzed with the following result: —

0.4869 gram of the salt gave 0.0478 gram of zincic oxide.

| | Calculated for $[C_6H_2(NO_2)_3C(COOC_2H_5)_2]_2Zn$. | Found. |
|---|---|---|
| Zinc | 8.07 | 7.88 |

*Properties.* — The zinc salt forms a reddish brown crystalline mass, essentially insoluble in water, but very hygroscopic. Like the barium salt it explodes easily, if heated with strong sulphuric acid, and therefore the same precautions must be used in analyzing it which were recommended in the case of the barium salt.

*Copper Salt.* — This salt was made by mixing aqueous solutions of cupric sulphate and the ammonium salt of the ester. It was purified by washing with water, and after drying at 100° gave the following result on analysis: —

0.3012 gram of the salt gave 0.0291 gram of cupric oxide.

| | Calculated for $[C_6H_2(NO_2)_3C(COOC_2H_5)_2]_2Cu$. | Found. |
|---|---|---|
| Copper | 7.92 | 7.72 |

*Properties.* — The copper salt is a brownish red powder, essentially insoluble in water, it resembles the barium and zinc salts in being very hygroscopic, and exploding easily, when heated with strong sulphuric acid.

### *Action of Nitric Acid on Trinitrophenylmalonic Ester.*

The action of nitric acid upon this substance is similar to its action with the bromtrinitrophenylmalonic ester,* that is, the nitrite or the substituted tartronic ester is obtained according to the length of the treatment.

### *Nitrite of Trinitrophenylmalonic Ester,*
### $C_6H_2(NO_2)_3CONO(COOC_2H_5)_2$.

Two grams of the trinitrophenylmalonic ester were heated on the steam bath with about 15 c.c. of common strong nitric acid. After three minutes the ester had melted to a clear red oily globule, and the entire liquid had taken on a reddish color. If the process was continued for two minutes more, the globule went into solution. The heating should not be continued beyond this point; in fact, it can be stopped to advantage even as soon as the globule of the melted substance is formed. If all the organic matter had gone into solution, reddish crystals separated in large quantity, as the liquid cooled, which were purified by washing with water and several crystallizations from alcohol, until they showed the constant melting point 109°. The globule, if the process was stopped before it disappeared, was allowed to solidify, and then purified in the same way. The substance was dried *in vacuo,* and analyzed with the following result: —

0.2190 gram of the substance gave 25.8 c.c. of nitrogen, at a temperature of 20° and a pressure of 760.8 mm.

| | Calculated for $C_6H_2(NO_2)_3CNO_2(COOC_2H_5)_2$. | Found. |
|---|---|---|
| Nitrogen | 13.46 | 13.46 |

### *Properties of the Nitrite of Trinitrophenylmalonic Ester.*

It crystallizes in long flat white prisms, apparently belonging to the monoclinic system, usually terminated by two planes at an obtuse angle to each other, but sometimes only by a single plane. It melts at 109° with

* These Proceedings, XXVI. 72.

decomposition, as shown by the appearance of a red color. It is easily soluble in ethyl, or methyl alcohol, or in chloroform, ether, benzol, glacial acetic acid, or acetone; nearly insoluble in carbonic disulphide; essentially insoluble in water, when cold, very slightly soluble in hot water, giving a pink solution. The three strong acids have no apparent action with it in the cold; strong sulphuric acid, when hot, decomposes it, as shown by the dark color produced and the evolution of gas; strong nitric acid, when hot, converts it into the corresponding tartronic ester. Alkalies have no action upon it at first, but gradually decompose it in the cold with the formation of a red solution; this action is much hastened by heat, but we have made no attempt to isolate the uninviting product.

In all these respects the nitrite of trinitrophenylmalonic ester resembles the nitrite of bromtrinitrophenylmalonic ester,* but we have not succeeded in converting the former into the corresponding tartronic ester by decomposition by heat, as was done with the latter. No crystalline substance could be obtained from the viscous red product of the fusion.

*Trinitrophenyltartronic Ester*, $C_6H_2(NO_2)_3COH(COOC_2H_5)_2$.

This substance was obtained by long continued action of hot nitric acid on trinitrophenylmalonic ester, or by the action of the same reagent on the nitrite just described. Two grams of trinitrophenylmalonic ester were warmed in a porcelain dish on the water bath with about 15 c.c. of common strong nitric acid, more acid being added from time to time to take the place of what evaporated. To secure the complete formation of the tartronic ester, the heating should be continued for five hours. If the acid solution was not too concentrated, it deposited on cooling long needles of a pink color arranged in rosettes; stronger solutions gave a more or less red solid cake of the same compound. It was purified by washing with water, and two recrystallizations from alcohol by cooling, when it showed the constant melting point 117°, and after drying *in vacuo* was analyzed with the following results: —

I. 0.2129 gram of the substance gave 20.8 c.c. of nitrogen at a temperature of 21° and a pressure of 769.7 mm.

II. 0.2051 gram gave 20.3 c.c. of nitrogen at a temperature of 25° and a pressure of 750.3 mm.

| | Calculated for $C_6H_2(NO_2)_3COH(COOC_2H_5)_2$. | Found. I. | Found. II. |
|---|---|---|---|
| Nitrogen | 10.85 | 11.24 | 10.87 |

* These Proceedings, XXVI. 74.

The analysis of this substance gave much trouble, because of the ease with which it exploded, but the difficulties were overcome by mixing it with a large amount of cupric oxide, and heating very carefully.

*Properties of Trinitrophenyltartronic Ester.* — It forms white fluffy needles in clusters like sheaves or even circles. Under the microscope the crystals are seen to be slender prisms terminated by a single plane at an oblique angle. Its melting point is 117°. It is easily soluble in ethyl, or methyl alcohol, in fact the hot concentrated solution in ethyl-alcohol is so strong that it solidifies nearly completely on cooling. It is also easily soluble in ether, benzol, chloroform, or acetone; soluble in glacial acetic acid; somewhat soluble in carbonic disulphide; soluble with difficulty in ligroine; insoluble in cold water, slightly soluble with decomposition in hot, forming a reddish solution. The three strong acids have no apparent effect on it in the cold, but hot strong sulphuric acid decomposes it, giving a dark color and an evolution of gas. Alkalies give with it at once dark blood-red solutions probably containing its salts, but these decompose rapidly, turning dirty brown, and we have not succeeded in isolating the salts themselves, or any definite compounds from their decomposition products.

### *Trinitrophenylacetyltartronic Ester,*
### $C_6H_2(NO_2)_3C(OCOCH_3)(COOC_2H_5)_2$.

Acetylchloride dissolves trinitrophenyltartronic ester easily, but does not react with it either at ordinary temperatures, or when heated on the steam bath in open vessels. We accordingly proceeded as follows: Three grams of trinitrophenyltartronic ester were heated with 15 to 20 c.c. of acetylchloride in a sealed tube to 110° for five or six hours. Care was taken that the temperature did not go too high, as at 140° a blackish decomposition product was also formed, which made the purification of the product more difficult. On evaporating off the excess of acetylchloride white crystals separated, which were purified by crystallization from alcohol until they showed a constant melting point of 125°, when they were dried *in vacuo*, and analyzed with the following result: —

0.2201 gram of the substance gave 19.4 c.c. of nitrogen at a temperature of 24° and a pressure of 761.6 mm.

| | Calculated for $C_6H_2(NO_2)_3COC_2H_3O(COOC_2H_5)_2$. | Found. |
|---|---|---|
| Nitrogen | 9.79 | 9.88 |

*Properties of Trinitrophenylacetyltartronic Ester.* — It forms white flat rather broad prisms, or perhaps they should be called tables, terminated

by two planes, and apparently belonging to the monoclinic system. It melts at 125°, and is easily soluble in ethyl or methyl alcohol, benzol, chloroform, or acetone; somewhat soluble in ether, less so in carbonic disulphide; soluble in glacial acetic acid; insoluble in ligroine; insoluble in cold water, slightly soluble in hot, forming a pink solution. Strong hydrochloric acid does not dissolve it. Nitric acid when hot dissolves it apparently without decomposition. Sulphuric acid dissolves it, and decomposes it, when heated. Alkalies have no effect on it in the cold, but, if heated with it, form the red salts of its decomposition product.

The benzoyl derivative of trinitrophenyltartronic ester was also made, but the close of the academic year prevented us from getting a satisfactory analysis of it. It was made by heating the tartronic ester with benzoylchloride in a sealed tube to 110° for four or five hours. On evaporating off the excess of benzoylchloride, it was obtained in white crystals, which were purified by recrystallization from alcohol until they showed the constant melting point 152°.

### *Saponification of Trinitrophenylmalonic Ester.*

In all these experiments the modification melting at 64° was used. The method of saponification adopted was that which had given such excellent results with the other substituted malonic esters studied in this laboratory, that is, the action of sulphuric acid diluted to a specific gravity of 1.44. Five grams of trinitrophenylmalonic ester were mixed with 100 c.c. of this acid, and the mixture boiled in a flask with a return condenser. The ester melted almost immediately to a straw-colored oily liquid, which gradually decomposed with evolution of gas, and finally was completely dissolved. This usually took place in from one and a half to two and a half hours, and showed that the reaction had come to an end. During the earlier part of the boiling the liquid appearing in the condenser had a pinkish color, but this disappeared later in the process. As soon as all the ester had dissolved, the liquid was allowed to cool, when it deposited a bulky precipitate made up of yellowish white needles. This substance consisted of the trinitrophenylacetic acid, and was purified in the way described in the following paragraph.

*Trinitrophenylacetic Acid*, $C_6H_2(NO_2)_3CH_2COOH$. — The purification of this substance cannot be effected by crystallization from alcohol or water, as either of these solvents converts it into the corresponding substituted toluol $C_6H_2(NO_2)_3CH_3$. We tried at first as a solvent water containing a small amount of sulphuric acid, since this had given excellent

results with bromdinitrophenylacetic acid;* but, whereas with that substance a few drops of sulphuric acid were sufficient to prevent the formation of the substituted toluol, we found that even one per cent of acid did not produce this effect with the trinitrophenylacetic acid, and that the amount must be raised to five per cent to insure perfect safety. Fortunately it was not necessary to use this rather strongly acidified water, as benzol proved to be an excellent solvent for the substance. Accordingly the crystals, which formed the product of the saponification (see the preceding section), were filtered from the sulphuric acid through glass wool, washed with water, dried, and recrystallized from benzol until they showed the constant melting point 161°, when they were dried at 100°, and analyzed with the following results: —

I. 0.2020 gram of the substance gave 28.2 c.c. of nitrogen at a temperature of 22° and a pressure of 750.8 mm.

II. 0.2093 gram of the substance gave 28.4 c.c. of nitrogen at a temperature of 20° and a pressure of 758.3 mm.

| | Calculated for $C_6H_2(NO_2)_3CH_2COOH$. | Found. I. | II. |
|---|---|---|---|
| Nitrogen | 15.50 | 15.59 | 15.46 |

*Properties of Trinitrophenylacetic Acid.* — It crystallizes from benzol in short needles arranged in sheaf-shaped bunches, and melts at 161°. As at first prepared it is white, but it turns pink on standing, even when in a corked tube, and this change is due to decomposition, as it is accompanied by an alteration in the melting point. It dissolves in ethyl or methyl-alcohol with a pink color, but this solution produces a decomposition, the trinitrophenylacetic acid losing carbonic dioxide and forming trinitrotoluol, which is left in a nearly pure state on the evaporation of the solvent. It was recognized by its melting point, 81°. Willbrand † gives 82°, Mills ‡ 78°.84 and 80°.52. (It is possible that further crystallization might have raised the melting point of our specimen to 82°.) The trinitrophenylacetic acid, therefore, is less stable than the bromdinitrophenylacetic acid, as two evaporations with alcohol were necessary to convert this entirely into the corresponding bromdinitrotoluol. One crystallization of the trinitrophenylacetic acid from boiling water was sufficient also to form the trinitrotoluol, and, as has been already said, the addition of five per cent of sulphuric acid was necessary to prevent this action. The aqueous solution had a pink color like that of the alcoholic solution, but we have not succeeded in discovering the cause of this color-

* These Proceedings, XXIV. 241.
† Ann. Chem., CXXVIII. 178.
‡ Phil. Mag., [5], XIV. 27.

ation, which disappears from the solutions, as the substituted toluol is purified by recrystallization. The solvents which follow dissolve the trinitrophenylacetic acid without decomposition; easily soluble in ether, glacial acetic acid, acetone, or ligroine; soluble in chloroform, less so in benzol or carbonic disulphide. The best solvent for it is benzol. The three strong acids seem to dissolve it without decomposition; it is more soluble in nitric acid or sulphuric acid than in hydrochloric acid. Alkalies dissolve it easily, forming deep blood-red solutions of its salts, but we have not yet succeeded in bringing any of these salts into a state fit for analysis.

### *Attempts to Make Ditrinitrophenylmalonic Ester.*

Dittrich,* in his work on the action of picrylchloride on sodium acetacetic ester, obtained without difficulty a ditrinitrophenylacetacetic ester; in fact this substance occurred as a secondary product in his preparations of trinitrophenylacetacetic ester, when he used the reagents in molecular proportions. It seems strange, therefore, that we have never observed the formation of a ditrinitrophenylmalonic ester as a secondary product in any of our preparations of the mono substituted ester. In the hope of preparing this substance (ditrinitrophenylmalonic ester) we converted 5 grams of the trinitrophenylmalonic ester into its sodium salt by treatment with the sodic ethylate from 0.31 gram of sodium, and then treated it with 3.4 grams of picrylchloride. The mixture was allowed to stand at ordinary temperatures over night, and, as no apparent change had taken place, it was divided into two portions, one of which was heated on the steam bath until it turned brown, and the other allowed to stand two weeks, when it had also turned brown, and deposited crystals of sodic chloride. The brown solutions, whether obtained by heating or by standing, yielded sodic picrate and a brown viscous mass, from which nothing fit for analysis could be isolated. A repetition of the experiment under other conditions gave the same result. It seems, therefore, that picrylchloride brings about a deep seated decomposition, when it acts on the sodium salt of the trinitrophenylmalonic ester, as the ditrinitrophenylmalonic ester would be without doubt a well crystallized compound. The products of this reaction recall Dittrich's description of the substances obtained by him from the action of picrylchloride on sodium malonic ester (pikrinsaures Natrium neben schmierigen Zersetzungs-producten des Malonsäureester), and it may be that the presence of an excess of picryl-

* Ber. d. chem. Ges., XXIII. 2720.

chloride was the cause of his failure to obtain trinitrophenylmalonic ester, although this does not appear from the statement in his papers.

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Some experiments on the action of aniline on trinitrophenylbrommalonic ester yielded only viscous unmanageable products; and boiling it with water gave no more promising results.

We have also tried several times to detect the presence of trinitrobenzol in the secondary products of the action of sodium malonic ester on picrylchloride, but without success. It seems, therefore, that the replacement of the chlorine of the picrylchloride by hydrogen does not take place under these conditions to any great extent, if it occurs at all.